



THE UNIVERSITY *of* EDINBURGH

## Edinburgh Research Explorer

### Accelerated degradation of MOFs under flue gas conditions

**Citation for published version:**

Mangano, E, Kahr, J, Wright, P & Brandani, S 2016, 'Accelerated degradation of MOFs under flue gas conditions', *Faraday Discussions*. <https://doi.org/10.1039/C6FD00045B>

**Digital Object Identifier (DOI):**

[10.1039/C6FD00045B](https://doi.org/10.1039/C6FD00045B)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Peer reviewed version

**Published In:**

Faraday Discussions

**General rights**

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

**Take down policy**

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact [openaccess@ed.ac.uk](mailto:openaccess@ed.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.



# Accelerated degradation of MOFs under flue gas conditions

E. Mangano<sup>a</sup>, J. Kahr<sup>b</sup>, P. A. Wright<sup>b</sup> and S. Brandani<sup>a,\*</sup>

<sup>a</sup> Institute for Materials and Processes, University of Edinburgh, The King's Buildings, Edinburgh EH9 3FB, UK

<sup>b</sup> EaStCHEM School of Chemistry, University of St. Andrews, Purdie Building, North Haugh, St Andrews, Fife KY16 9ST, UK

## Abstract

The zero length column (ZLC) technique is used to investigate the stability of Mg- and Ni-CPO-27 metal organic framework (MOF) crystals to the presence of water and humid flue gas. The design of the ZLC enables the stability test to be conducted over a considerably shorter time period and with lower gas consumption than other conventional techniques. A key advantage over other experimental methods to test the stability of adsorbents is the fact that the ZLC allows to quantify the amount adsorbed of every component present in the gas mixture. The developed protocol is based on a two-stage stability test. The samples were first exposed to a humid carbon dioxide and helium mixture in order to study the effect of water on the carbon dioxide adsorption capacity of the samples. In the second stage the samples were exposed to a flue gas mixture containing water. From the preliminary water stability test, the Ni-sample exhibited the highest tolerance to the presence of water, retaining approximately 85% of its pristine CO<sub>2</sub> capacity. The Mg-MOFs deactivated rapidly in the presence of water. The Ni-CPO-27 was then selected for the second stage of the protocol in which the material was exposed to the wet flue gas. The sample showed an initial drop in the CO<sub>2</sub> capacity after the first exposure to the wet flue gas followed by a stabilisation of the performance over several cycles.

\*Corresponding author: s.brandani@ed.ac.uk

## Introduction

Metal organic frameworks (MOFs) consist of organic-inorganic hybrid networks formed by metal to ligand bonds.<sup>1</sup> The possibility of creating thousands of different structures by changing the nature and the combination of the main building blocks to design novel adsorbents for carbon capture applications has attracted the interest of researchers.<sup>2</sup> Among the several different types of MOF samples investigated the CPO-27 series (also known as MOF-74 and DOBDC) and its polymorphs have shown great promise for post combustion carbon capture with relatively high uptake at low CO<sub>2</sub> partial pressures.<sup>3</sup>

In real applications the CO<sub>2</sub> has to be captured from flue gas streams which contain contaminants such as water (10-15%), SO<sub>2</sub> (0.1-0.5%) and NO (0.01-0.05%).<sup>4</sup> These contaminants can dramatically affect the adsorption performance of the adsorbent. Despite the large number of studies in the literature on the fundamental adsorption properties of MOFs, there are very few studies on the effect of SO<sub>2</sub> and NO on the stability of these materials and on their CO<sub>2</sub> adsorption capacity.<sup>5-8</sup> In a recent review,<sup>9</sup> Burtch et al. define the guidelines to ascertain the stability of MOFs for different applications. For industrial gas separation, the testing conditions for the stability are described as “cyclic exposure to relevant gas mixture; subsequent regeneration via pressure or temperature swing”.

LeVan et al.<sup>5</sup> investigated the effect of water on the adsorption of CO<sub>2</sub> on Ni- CPO-27 and HKUST-1 at the conditions of interest for CO<sub>2</sub> capture from flue gas. A closed loop volumetric apparatus was used to measure the pure component isotherms and to study the effect of water on the CO<sub>2</sub> adsorption. The system measures the CO<sub>2</sub> isotherms up to 1 bar before and after the conditioning of the sample in presence of different H<sub>2</sub>O loadings. The system is connected to a gas chromatograph to monitor the CO<sub>2</sub> concentration in the gas phase. Ni-CPO-27 exhibited a higher degradation resistance maintaining the majority of its CO<sub>2</sub> capacity after several cycles of water exposure and thermal regenerations. On the other hand, the study showed that small amount of H<sub>2</sub>O may even increase the CO<sub>2</sub> capacity for HKUST-1. In a more recent work<sup>6</sup> the same apparatus has been used to investigate the stability of Mg- and Ni-CPO-27 using humid and dry flue gas. First the stability towards steaming was investigated. After steaming for 2h the Mg sample, being more prone to oxidation, showed a CO<sub>2</sub> capacity 51% lower than the original one. On the other hand the Ni sample was barely affected by the steaming process. For this reason the Ni-MOF sample was then selected for the stability tests with a synthetic flue gas. The adsorbent was exposed to dry and wet flue gas for 72 h before being regenerated and tested for CO<sub>2</sub> capacity. The CO<sub>2</sub> isotherms after the conditioning show very little effect from the dry flue gas exposure while the sample loses less than 10% of the original capacity after the wet flue gas conditioning.

Breakthrough experiments on Ni- CPO-27 using dry and wet CO<sub>2</sub> and N<sub>2</sub><sup>10</sup> proved that H<sub>2</sub>O molecules interact specifically with the strong CO<sub>2</sub> adsorption sites affecting permanently the performance of the material. The permanent loss of adsorption capacity for MOFs after exposure to water has been also associated to structural degradation, with a significant loss of crystallinity and pore volume.<sup>11, 12</sup>

Similarly, Kizzie et al.<sup>13</sup> used breakthrough experiments to study the effect of water on different polymorphs of CPO-27 samples (Mg-, Zn-, Ni-, and Co-CPO-27). The samples were exposed to mixtures of CO<sub>2</sub> and N<sub>2</sub> with different humidity content and successively thermally regenerated to measure the CO<sub>2</sub> capacity. Despite the higher original CO<sub>2</sub> capacity, the Mg- sample exhibited the highest loss of capacity on exposure to water. The Co- and Ni- CPO-27 were the most stable samples retaining 85% and 60% of their original capacity respectively, after exposure to a mixture with a relative humidity of 70%.

Stability of several types of MOFs has been studied using a high-throughput sorption system.<sup>7,8</sup> The apparatus allows to measure gas adsorption for up to 36 samples in parallel by following the pressure decay with time in each sample chamber. For the stability tests the samples are exposed first to humid air and then to humid acid mixtures containing ppm levels of SO<sub>2</sub> and NO<sub>2</sub>. Samples were exposed for a minimum of 2 days (short term) to a maximum of 5 days (long term). After each conditioning CO<sub>2</sub> adsorption was measured. While the system has the clear advantage of parallel testing of multiple samples, on the other hand, by monitoring the total pressure in each chamber it is not possible to quantify the amount adsorbed for each component of the gas mixture, H<sub>2</sub>O, SO<sub>2</sub> and NO<sub>2</sub>. CO<sub>2</sub> capacities for the samples tested are generally slightly affected by the humid air and acid gasses exposures, while only one sample, Ni-NIC, showed clear improvement of performance after the conditionings. These tests were carried out as a single exposure, so no data are available for the stability over several cycles.

The effect of the presence of water or acid gasses on the CO<sub>2</sub> capacity of MOFs has been investigated by many researchers. Even though these tests cannot be defined as stability tests, they often provide a useful insight on the possible degradation mechanisms caused by these contaminants. Several CPO-27 polymorphs were used by Glover et al.<sup>14</sup> to investigate how the presence of water affects the adsorption of different toxic gases, including SO<sub>2</sub>. Among all the samples tested Ni-CPO-27 showed the lowest adsorption capacity for both water and SO<sub>2</sub>. The study also reported, that for all the samples, the presence of water significantly reduced the uptake of toxic gases. This indicates that there is competitive adsorption of these adsorbates on the same sites. The adsorption of NO has also been studied and the reported data show that there is a significant uptake on Ni and Co-CPO-27.<sup>15-18</sup>

In support of the experimental data, some molecular modelling studies<sup>19, 20</sup> investigating the effect of the main contaminants contained in the flue gas on the adsorption of CO<sub>2</sub> on MOFs have also been presented. From these studies it emerged that the presence of NO does not dramatically affect the CO<sub>2</sub> adsorption performance of certain MOF materials (CPO-27 for example) while it has a higher impact on other MOF varieties (HKUST-1). On the other hand the presence of water, which deteriorates the performance of CPO-27, seems to improve the CO<sub>2</sub> uptake for HKUST-1 at low pressure, mainly due to an increase in the electrostatic interactions.<sup>19</sup> With regard to SO<sub>2</sub>, despite its very low content in the flue gas streams, it has probably the largest detrimental effect on the MOF materials. Computational studies have shown that in presence of water SO<sub>2</sub> reacts with the metal sites forming hydrates which bind extremely strongly with the open metal sites. Removal of these species would require temperatures of 500 – 600 K, which makes the adsorption of these compounds practically irreversible, causing a permanent loss of the adsorption capacity. A similar behaviour is observed for NO and its hydrate forms. In the case of the CPO-27 MOF types, the enthalpies of adsorption of NO<sub>x</sub> hydrates are comparable to the enthalpy of adsorption of CO<sub>2</sub>, making the poisoning effect from NO<sub>x</sub> less significant than SO<sub>x</sub>.<sup>20</sup>

Here we present the use of the zero length column (ZLC) technique for the study of the stability of Mg- and Ni-CPO-27 under conditions of interest for post-combustion carbon capture. Compared to the other techniques previously used to conduct similar experiments the ZLC provides the key advantage that only a very small amount of adsorbent (10-15 mg) is required. Therefore, in a few hours, a volume of flue gas per mass of adsorbent can be passed over the adsorbent that is equivalent to several days or weeks of experiments if tested using conventional breakthrough or volumetric methods on much larger samples. This results in a protocol that “accelerates” the degradation dynamics giving rapid feedback when novel adsorbent materials are being developed. With the rapidly growing number of novel materials being proposed for carbon capture applications,

it is evident that the ZLC technique applied to test material stability is a very useful tool in the early stages of material development and selection. Here an additional advantage of ZLC systems is that with a mass spectrometer it is possible to monitor all the components of the gas mixture and quantify the amount adsorbed for each adsorbate in the gas phase. This allows in a very short time to determine the process requirements needed to improve the expected lifetime of novel adsorbents in carbon capture applications.

## Experimental

### Materials

The MOFs used in these experiments consists of two different types of Mg-CPO-27 and one of Ni-CPO-27. The samples were prepared by following the general procedure as described in the literature.<sup>21, 22</sup> In the case of Mg-CPO-27 the solvothermal synthesis was performed at 110 °C for 3 days and a Mg-nitrate (metal source) and 2,5-dihydroxyterephthalic acid were used. The material was activated by immersing the sample in water over a few days and heating in vacuum at 250 °C for 18 h. One of the Mg-CPO-27 sample was prepared using this procedure<sup>21</sup> (from this point on referred as Mg-CPO-27 (1)), while the other one was subjected to post-synthesis treatments using Ni and carboxyphosphonate acid as ligand (Mg-CPO-27 (2)). The synthesis procedure used for the preparation of the Ni-CPO-27 is that reported in the literature.<sup>22</sup> Full characterisation of the samples, including XRD patterns, is presented in an earlier contribution.<sup>23</sup>

### Measurements of CO<sub>2</sub> capacity

The ZLC consists of a 1/8" Swagelok union in which a very small amount of adsorbent (10-15 mg) is packed as monolayers between two sintered discs. The ZLC experiment is a chromatographic method which is based on following the desorption curve of a sample pre-equilibrated with a known gas mixture. Once the sample reaches equilibrium with the feed gas mixture the inlet flow is switched to a constant flowrate of carrier gas (generally He or N<sub>2</sub>) and the desorption profile is monitored. The small amount of sample and the small size of the column allow to have a system that behaves like a well-mixed cell with minimal external heat and mass transfer resistance and negligible pressure drop. A detailed description of the experimental system used in this study is provided in a recent publication.<sup>24</sup> For the specific measurements of CO<sub>2</sub> uptake for post-combustion capture from coal fired power plants the feed mixture contains 10% of CO<sub>2</sub> in helium (carrier). The feed mixture is prepared in a specifically designed dosing oven equipped with drying columns to ensure that any traces of water are removed from the gases entering the system. The outlet of the ZLC is connected online with a Dycor Ametek Benchtop quadrupole mass spectrometer with a custom-made inlet for a faster response. Figure 1 shows a simplified schematic diagram of the apparatus used in the experiments.

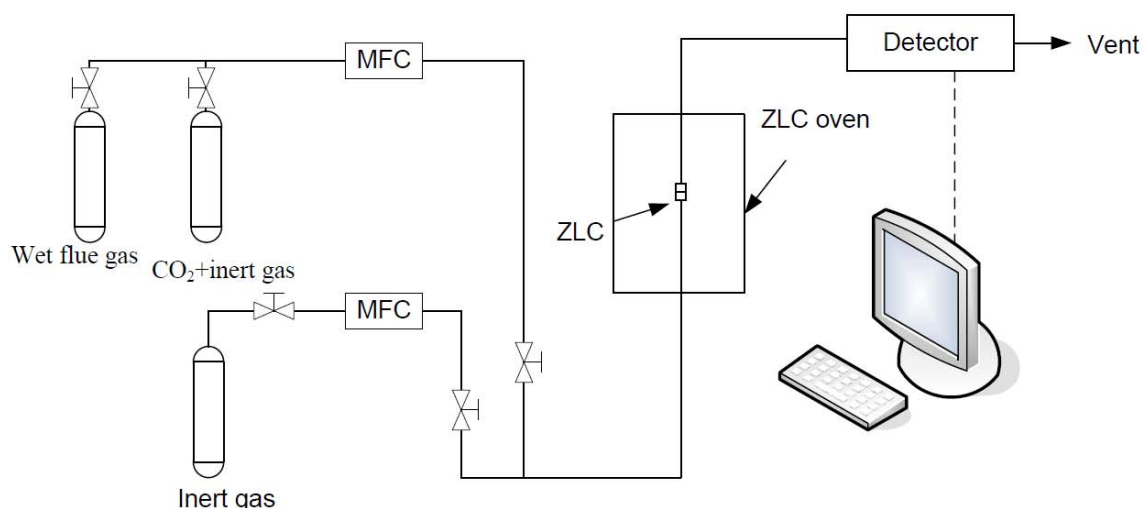


Figure 1: Schematic view of the ZLC apparatus.

Prior to each experiment the samples were regenerated overnight under helium flow at a temperature of 150°C and 250°C for the Ni and Mg samples respectively. The experimental conditions were chosen to be representative of the typical conditions for post-combustion capture: 35°C and 0.1 atm partial pressure of CO<sub>2</sub>. The amount of CO<sub>2</sub> adsorbed can be determined from a mass balance applied to the ZLC and can be obtained by numerical integration.<sup>24, 25</sup> Each experiment was repeated at different flowrates to confirm the adsorbed amount and to determine if the system is under equilibrium control conditions.<sup>26</sup>

### Stability tests

The basic principle of the stability test is to investigate the effect of contaminants on the CO<sub>2</sub> capacity of the adsorbent. In order to separate the effect of water from the other contaminants and also to minimise the total number of experiments a first stage is aimed at determining only the effect of water. Those materials that are stable in the presence of water are then considered for the second stage which uses a synthetic flue gas. In this study the experiments were performed in two stages.

ZLC columns used in this study were packed with: Ni-CPO-27 (13.7 mg), Mg-CPO-27(1) (6.8 mg), and Mg-CPO-27(2) (8.8 mg). The Mg samples were totally deactivated during the water stability cycles, for this reason, only the Ni sample was selected for the wet flue gas exposure. The flue gas exposure was also repeated on second column with a fresh sample of Ni-CPO-27(8.3 mg) to check the reproducibility of the results.

### Stage 1: Water stability test

The effect of the presence of water was investigated by exposing the sample to a mixture containing 1% of H<sub>2</sub>O (corresponding to a relative humidity of 17.8%), 16 % of CO<sub>2</sub> the balance given by the carrier gas, He. The concentration of CO<sub>2</sub> is representative of a typical dried flue gas stream from coal fired power plants. The concentration of water is deliberately set to a relatively low value given that in carbon capture applications of physical sorbents the gas stream has to be pre-dried.<sup>27</sup> Therefore, the purpose of our investigation is aimed at determining what happens if in a layered

adsorption bed a small amount of water migrates to the section where the MOF materials capture the CO<sub>2</sub>.

Particular care was given to the determination of the exact amounts of water added to the feed mixture. The water is introduced to the mixture using a specially designed capsule for liquids which is connected to the cylinders in the dosing oven. The water contained inside the capsule is evaporated into the mixing volumes by increasing the oven temperature. The system has also a pressure transducer which enables the pressure to be monitored during the evaporation. The difference between the weight of the capsule before and after the evaporation gives the exact amount of water introduced into the system; this can be cross-checked with the pressure read-out to verify that no condensation has occurred anywhere in the system, i.e. that no cold spots are present. Helium and CO<sub>2</sub> are then added in the correct proportions to make the desired mixture.

In the experimental protocol for the stability test, the sample is first exposed under flow (9.8 ml/min) to the wet mixture, then thermally regenerated and finally a ZLC experiment is performed to measure the capacity at 0.1 atm CO<sub>2</sub> as described above. The procedure is cyclically repeated until the sample remained either stable or significantly de-activated. Mg-CPO-27(2) was exposed to the wet flue gas for 6 hours. Due to the fast deactivation of the sample it was decided to reduce the exposure time to four hours for Mg-CPO-27(1). For the Ni sample the exposure time was gradually increased according to the following sequence: exposures 1, 2 and 3 for 2 hours, exposure 4 for 6 hours, exposure 5 for 12 hours, exposure 6 and 7 for 6 hours.

## Stage 2: Exposure to synthetic flue gas

The second stage of the stability test protocol consists in exposing the sample to a synthetic wet flue gas. The mixture in this case is prepared using a dry synthetic flue gas supplied by BOC containing 16% CO<sub>2</sub>, 100 ppm SO<sub>2</sub>, 10 ppm NO and N<sub>2</sub> as balance. The synthetic flue gas can only be supplied as a pressurised gas mixture without water present to avoid corrosion in the cylinder and pressure regulator. Water was added in the dosing oven to this mixture using the same procedure discussed in the water stability test.

To ensure complete equilibration with the components in the mixture, the samples were exposed for 5 hours to the wet flue gas under flow (3.8 ml/min) monitoring the exit compositions. The samples were then thermally regenerated under helium flow (5.5 ml/min) for two hours followed by a temperature ramp of 1 K per minute up to the regeneration temperature (150°C) and held at this temperature overnight. The total amounts desorbed can be calculated from a mass balance that includes the temperature programmed desorption step.<sup>28</sup> Finally a standard ZLC experiment was carried out to measure the CO<sub>2</sub> capacity as above.

There are multiple advantages to using the ZLC method to investigate the stability of the adsorbents. From the start of the protocol (i.e. when the column is packed) to the end, the sample is never removed from the system, thus reducing the impact of any external factors which may affect the results. The dosing oven enables multiple mixtures to be prepared and stored so that it is simple to switch from one feed mixture to the other, i.e. from one type of experiment to another. Thanks to the small amount of sample, several hours of exposure are equivalent to weeks or months of exposure in a scaled-up or industrial system. The result is a protocol which “accelerates” the deterioration cycle of the adsorption column enabling the life-time of adsorbents in real applications to be predicted. This also requires a significantly lower amount of gas compared to other

experimental methods, which is particularly relevant in this case since synthetic flue gas is a specialty gas and thus is quite expensive.

## Results

Figure 2 shows the results of the water stability test performed on the three CPO-27 samples as percentage of CO<sub>2</sub> capacity vs. the volume of water eluted per mass of sample.

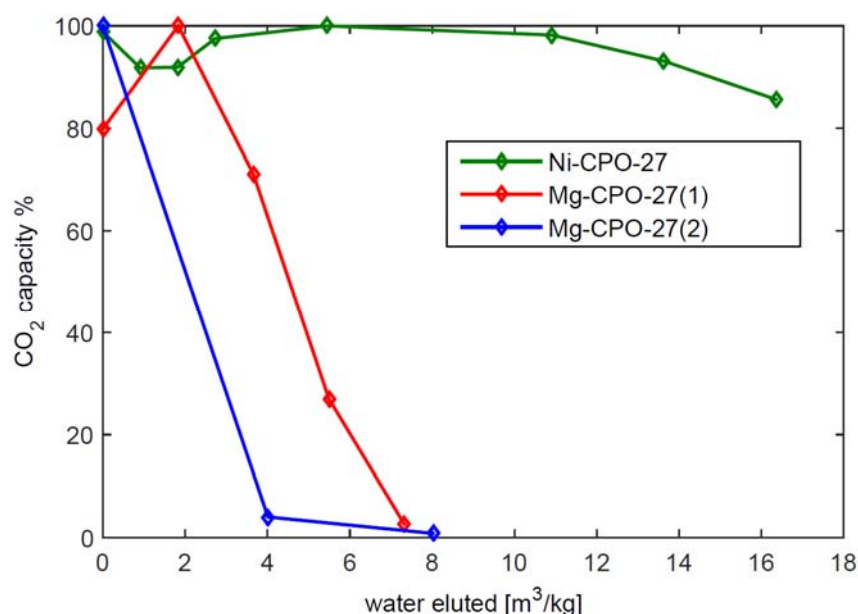


Figure 2: Deactivation trend in the water stability test for the Mg- and Ni-CPO-27.

The original CO<sub>2</sub> capacities of the fresh samples were 1.78 mol/kg for the Ni sample; 4.56 mol/kg for the Mg-CPO-27(2); and 3.7 mol/kg for the Mg-CPO-27(1). The CO<sub>2</sub> capacities measured on the samples are consistent with literature values of fully open CPO-27 structures with accessible unsaturated metal sites.<sup>29</sup>

From Figure 2 it can be seen that the Mg-MOF samples show very fast deactivation with most of the capacity lost after the first few cycles. It is interesting to note that the sample activated in water, Mg-CPO-27 (1), showed an increase in its CO<sub>2</sub> capacity after the first exposure to water. A possible explanation in this case is that the regeneration at high temperature helped to open pores which were not previously active. Once fully activated the sample starts to deactivate at a similar rate as the other Mg sample. Figure 3 shows the experimental ZLC desorption curves for the Mg-CPO-27 (1) activated in water after each exposure cycle.

Given that the CO<sub>2</sub> capacity is approximately proportional to the area under each curve,<sup>24</sup> Fig. 3a shows clearly that the material is deteriorating at each cycle. The Ft plot of the ZLC experiments clearly shows the overlap of the desorption curves at different flowrates. This indicates that the system is equilibrium controlled. This means that each point of the ZLC desorption curve is an equilibrium point and the CO<sub>2</sub> isotherms can be calculated from the mass balance.<sup>25</sup> In Figure 3b the isotherms calculated from the ZLC desorption curves are reported. After the first exposure to water the sample loses capacity mainly in the low concentration region (strong adsorption sites), while more capacity is gained in the high concentration region (weak adsorption sites), resulting in higher



total capacity. Similarly to what reported by Liu et al.<sup>5</sup>, it seems that the effect of the water is primarily on the strongest sites, while the weak sites, which were activated after a couple of thermal regeneration cycles, were responsible for the increase of the CO<sub>2</sub> uptake after the first exposure to water vapour.

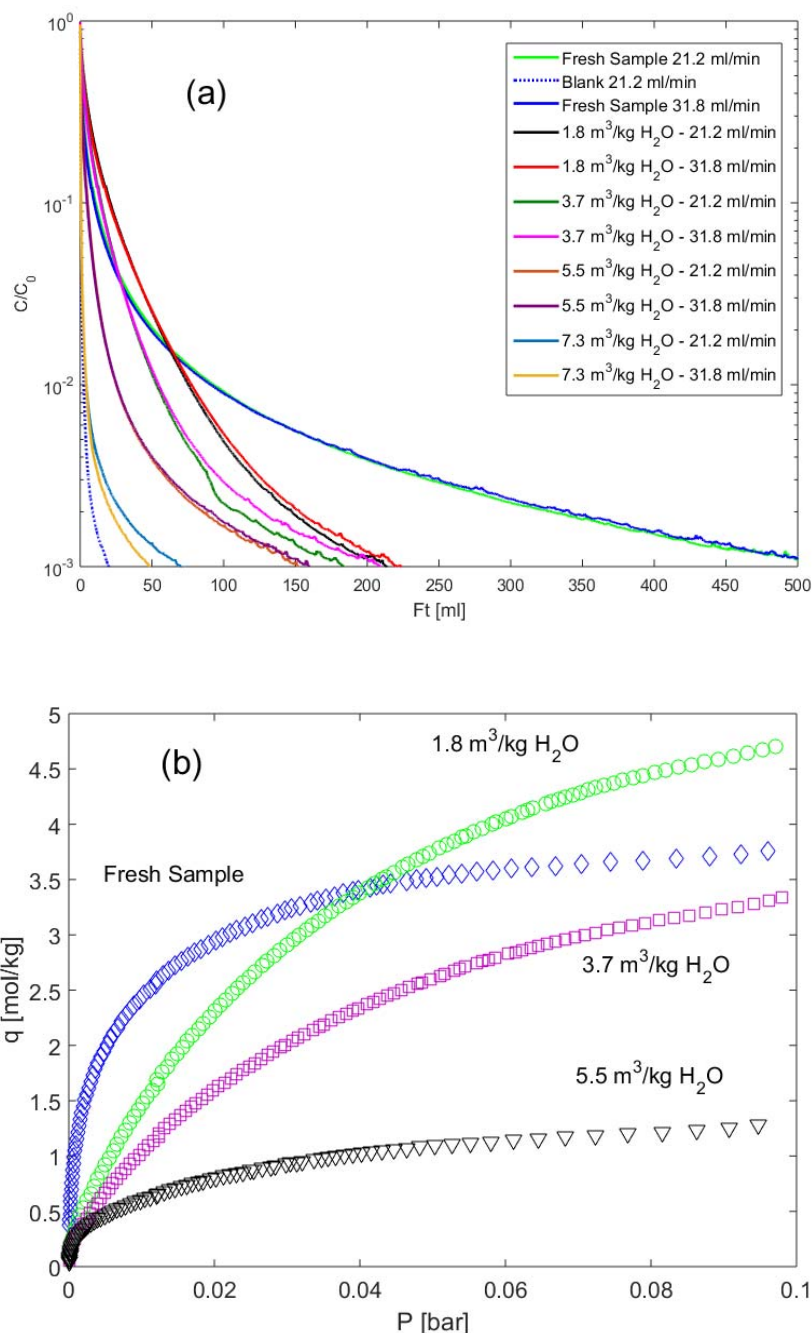


Figure 3: a) ZLC desorption curves after different exposures to water for Mg-CPO-27(1);  $T = 35^\circ\text{C}$ , flowrate = 31.75 ml/min. b) isotherms calculated from the ZLC curves at different water exposures

The Ni-CPO-27 is considerably more stable than the two samples of Mg-CPO-27. The sample loses adsorption capacity after the first two cycles, while it recovers the original CO<sub>2</sub> adsorption capacity

after the fifth cycle. After the fifth exposure the sample starts to deactivate slowly retaining about 85% of the original capacity at the end of the tests. The higher stability to water of Ni-MOF over the Mg type has been reported by other studies<sup>6, 13</sup>. Liu et al.<sup>6</sup> explain that this is possibly related to the standard reduction potential of the metal sites. Being  $Mg^{2+}$  a stronger reducing agent, it is more prone to react with water than  $Ni^{2+}$  causing a the loss of unsaturated metal centres, i.e. a permanent loss of capacity.<sup>6, 30</sup>

Having established that the Ni sample is stable to water, stability testing was extended to the second stage and the Ni-CPO-27 sample was subjected to the wet flue gas exposure. Figure 4 shows the raw signal acquired during the final wet flue gas exposure. The results show that  $CO_2$  and NO breakthrough almost immediately after the start of the adsorption step, while the breakthrough time for  $H_2O$  and  $SO_2$  is much higher. The  $CO_2$  signal shows clearly a roll-up: the  $CO_2$  initially adsorbed on the sample is pushed out by  $H_2O$ , which is adsorbed more strongly. This increases the  $CO_2$  concentration in the gas phase until  $H_2O$  finally breaks through. The strength of adsorption of each component is clearly visible also in the desorption step. After the start of the desorption  $CO_2$  and NO are completely desorbed in the first two hours of purging. No significant amount of NO is released during the heating step of the desorption confirming that the interaction energy for NO and its hydrates on CPO-27 MOFs is much lower than the one associated to the  $SO_2$ , resulting in a reversible adsorption process.<sup>20, 31-33</sup> This, combined to the low concentration originally present in the flue gas mixture (10 ppm) and the low amount adsorbed, allows to conclude that NO is not a major “poisoning” compound for this sample. The signals for  $H_2O$  and  $SO_2$ , on the other hand, show that a considerable amount is being desorbed at a higher temperature. This indicates that in a normal PSA cycle these components will be in practice irreversibly bound to the adsorbent. The main advantage of developing a ZLC-based methodology for the stability test is that it allows to check easily if the saturation for each component is achieved.

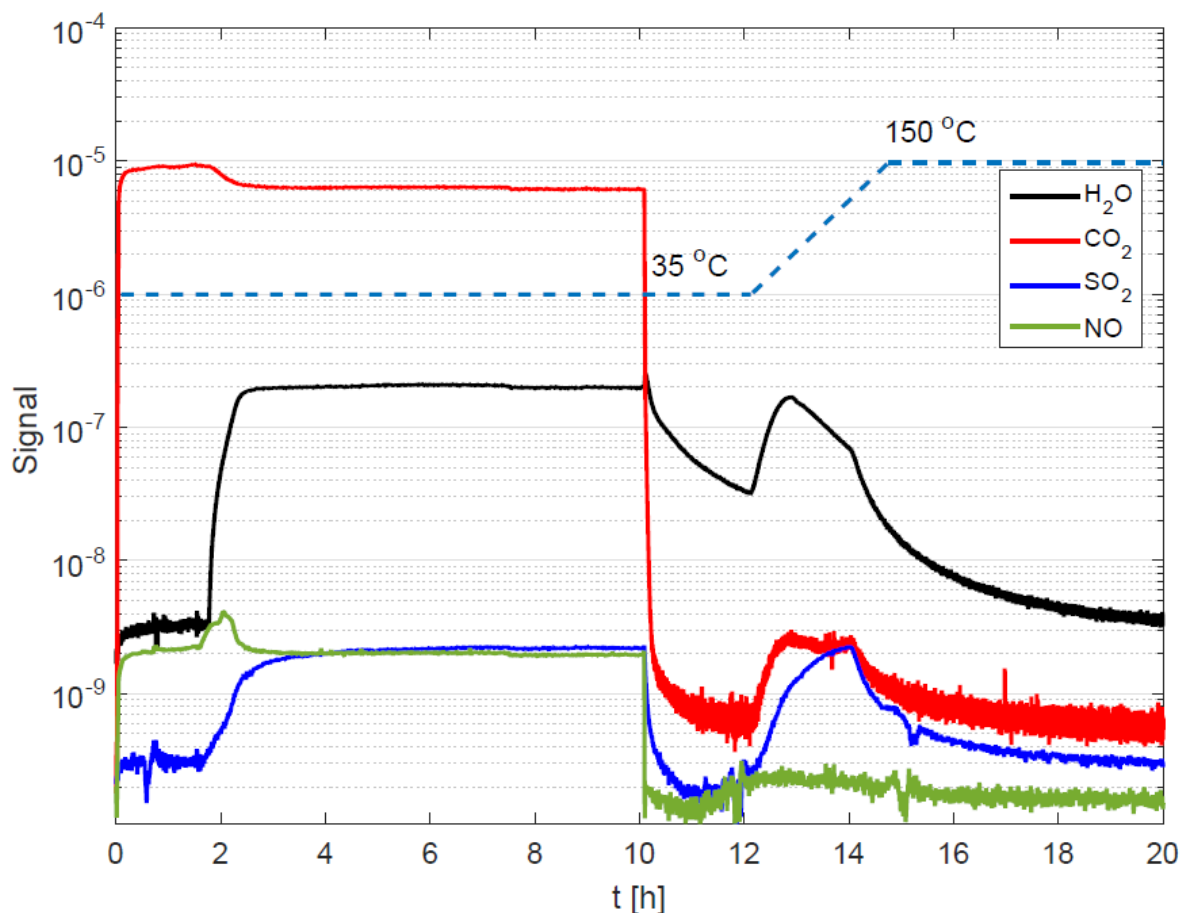


Figure 4: Example of signal acquired during the wet flue gas exposure on the Ni-CPO-27.

Figure 5 shows the normalised adsorption curves for  $\text{SO}_2$  at the different wet flue gas exposures. In this case the original raw signal is normalised as  $C/C_0$  in which  $C_0$  is the concentration of  $\text{SO}_2$  originally present in the flue gas mixture. At each exposure  $\text{SO}_2$  breaks through at earlier times and gradually approaches the original concentration. For symmetric adsorption curves, a quick way to estimate the first moment is by determining the time at which  $C/C_0 = 0.5$ .<sup>34</sup> For the case of  $\text{SO}_2$  the time required to reach more than 95% of the original concentration in the gas phase is about twice the first moment. In addition, because of the low flowrate and the small size of the column the pressure drop is negligible and it can be assumed that effects of kinetic resistance and gas bypass are minimised during the adsorption process. Based on these observations a simple criterion for complete saturation can be established by assuming that an amount of time equal to 3 times the first moment is required to fully saturate the sample. In Fig. 5 vertical lines identify the first moment and the times corresponding to 2 and 3 times its value. A similar criterion was used for the  $\text{H}_2\text{O}$  signal, as shown in Fig. 6. The curves obtained allow to determine the minimum amount of gas that needs to be contacted with the solid material in order to saturate the sample with  $\text{H}_2\text{O}$  and  $\text{SO}_2$  and allows to compare the results obtained by different stability studies. The total volume of  $\text{SO}_2$  used to saturate the system is about  $0.8 \text{ cm}^3$ , which means that, for each gram of adsorbent, at least  $58.3 \text{ cm}^3$  of  $\text{SO}_2$  are needed to achieve saturation (using the same criterion 100 times more would be needed for  $\text{H}_2\text{O}$ ). The volume of the adsorption bed used by Liu et al. ( $0.9 \text{ mL}$ )<sup>6</sup> is about 20 times larger than the ZLC system used in this study and for the 72 h flue gas exposure the volume of  $\text{SO}_2$  circulated is about  $1.3 \text{ cm}^3$ , which is approximately 1/45 of the amount that would be needed to

saturate the sample. This means that the system was still far from saturation which would possibly explain why the  $\text{CO}_2$  capacity is only slightly affected by the flue gas exposure.<sup>6</sup> The capability of monitoring each component in flue gas mixture, and hence, estimating when full saturation is reached represents a key element to assess the stability of an adsorbent in aggressive conditions. What is important is to evaluate is not the length of exposure, but how much of the impurities and water are actually adsorbed on the solid.

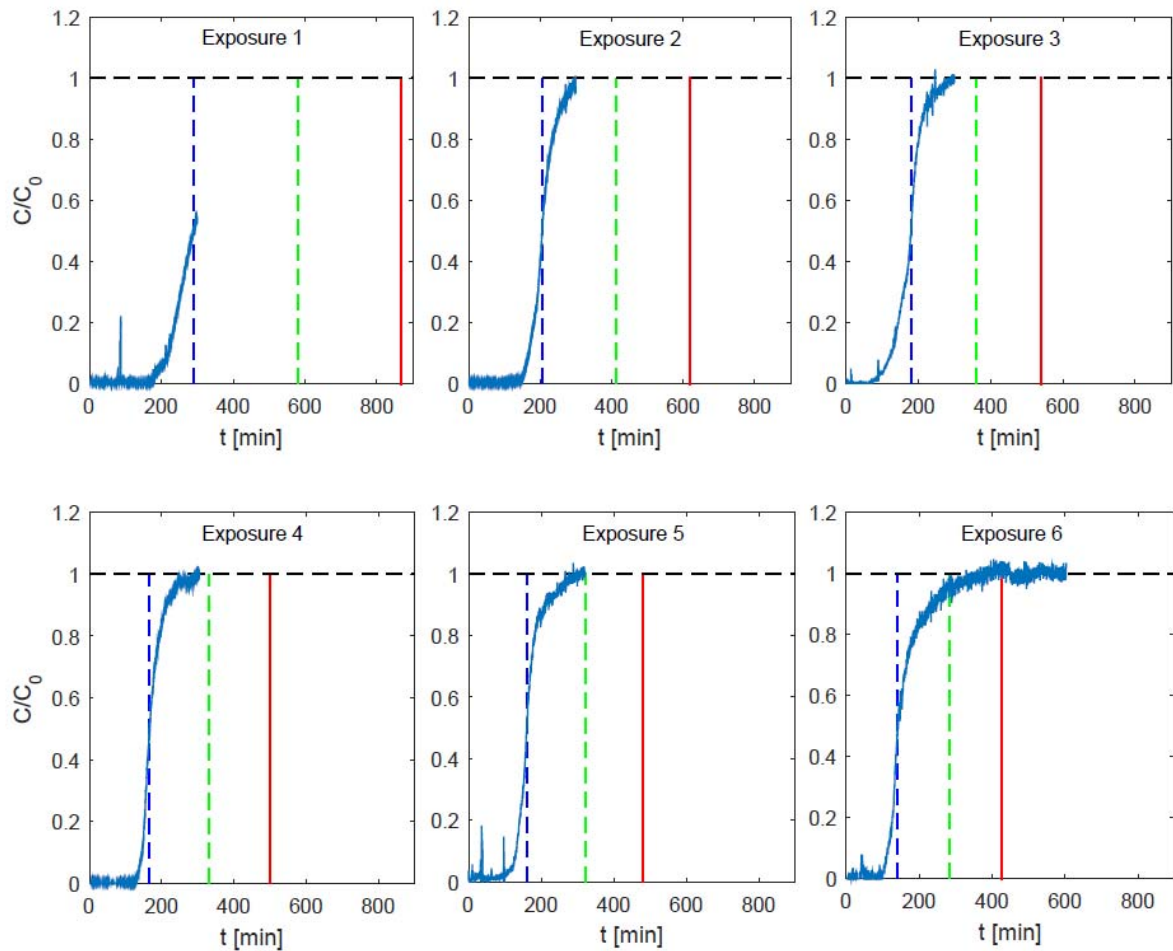


Figure 5: Experimental adsorption curves for  $\text{SO}_2$ . Vertical blue, green and red lines indicate first moment, and the times corresponding to 2 and 3 times the first moment respectively.

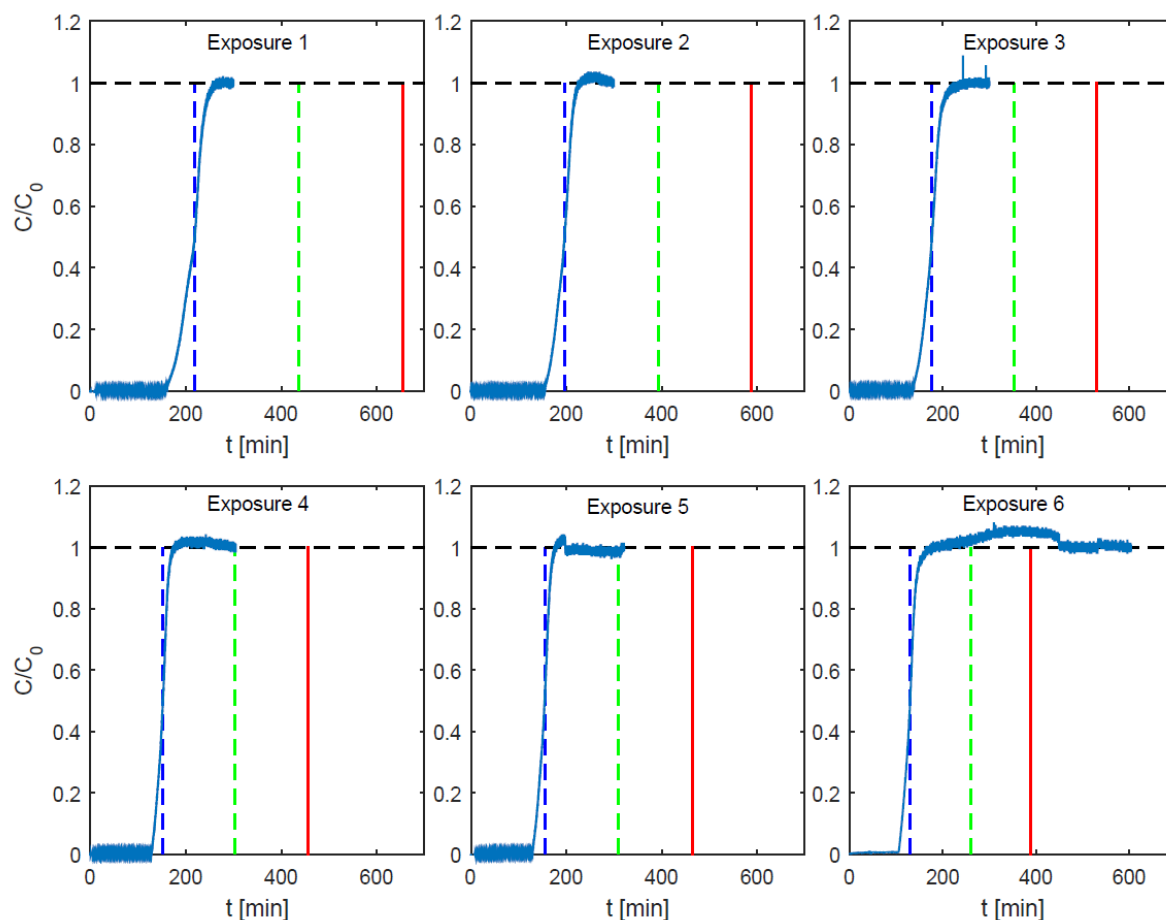


Figure 6: Experimental adsorption curves for H<sub>2</sub>O. Vertical blue, green and red lines indicate first moment, and the times corresponding to 2 and 3 times the first moment respectively.

Figure 7 shows the trend in the adsorbed amount of H<sub>2</sub>O, SO<sub>2</sub> and CO<sub>2</sub> (original sample and fresh sample) at each exposure. For H<sub>2</sub>O and SO<sub>2</sub>, the values are shown here as percentage relative to the maximum capacity (first exposure). As seen in Figs 5 and 6, after each exposure SO<sub>2</sub> and H<sub>2</sub>O adsorb gradually less indicating that adsorption sites are irreversibly deactivated during the exposure to the acid mixture. This is probably due to the formation of SO<sub>2</sub> hydrates which, due to the high interaction energy, are irreversibly adsorbed on the metal sites causing a permanent loss of capacity.<sup>20</sup> At each exposure the amount of SO<sub>2</sub> adsorbed decreases until it reaches a stable value at around 60% of the materials' maximum capacity. To ensure that this limit was not dependent on the equilibration time a final exposure was run with a contacting time of 10 hours. The final experiment confirms that no further deactivation occurs. In the presence of water the SO<sub>2</sub> appears to deactivate a particular type of adsorption site but does not deactivate completely the material. The rest of the sites show a higher resistance to the flue gas contaminants and, as a result, a stabilisation in the capacity was observed.

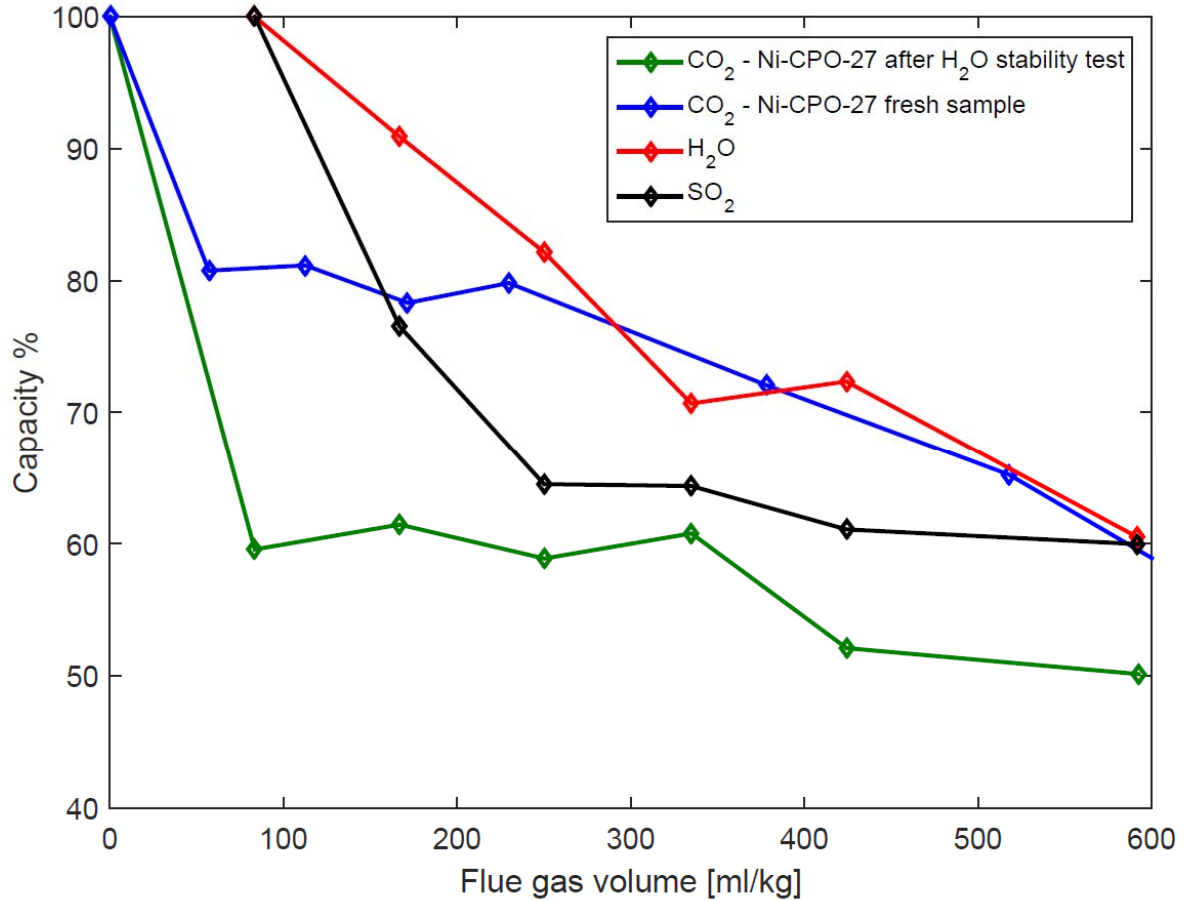


Figure 7: Trend of the SO<sub>2</sub> and H<sub>2</sub>O uptake during the cycles of exposure to the wet flue gas.

The deactivation of the material is reflected also in the trend of the CO<sub>2</sub> capacity of the sample, shown in Fig. 7. The figure includes the results for the original sample which was exposed to water and to the wet flue gas and also for a fresh sample which was treated directly with the wet flue gas. The capacity of the fresh sample before the conditioning was 1.68 mol/kg. The slight loss of CO<sub>2</sub> capacity is probably due to ageing due to storage, similarly to what has been reported by Liu et al.<sup>6</sup> In Fig 7, the CO<sub>2</sub> capacity of the first sample is normalised with that obtained after exposure to water. The trend in the CO<sub>2</sub> capacity during the flue gas exposure shows a significant drop in the uptake to a value slightly less than 60% of the initial capacity. In the successive exposures the sample loses progressively some capacity reaching approximately 50% of the original value.

For the second sample the contacting time between capacity measurements was reduced to two hours, due to the lower mass packed in the ZLC. Figure 7 shows that in this case the capacity loss is less pronounced at the start, but eventually with the same amount of exposure in terms of gas contact, also the fresh sample tends to reach approximately 50% of the original capacity. In both cases after each exposure the CO<sub>2</sub> uptake is reduced, meaning that a portion of the adsorption sites has been neutralised as a result of the contact with the flue gas mixture. At each exposure, also, the uptakes for H<sub>2</sub>O and SO<sub>2</sub> are reduced, indicating that the sites that had previously hosted these molecules are now unavailable for adsorption. Several studies have confirmed that CO<sub>2</sub>, H<sub>2</sub>O and SO<sub>2</sub> are competing on the same adsorption sites.<sup>14, 20, 32, 35, 36</sup> The fact that at the end of the conditioning

all gas components show about the same relative loss in capacity confirms that CO<sub>2</sub> adsorbs in the same sites in which SO<sub>2</sub> hydrates are formed and permanently bound.

## Conclusions

A novel experimental protocol to investigate of the stability of Mg and Ni-CPO-27 with respect to their exposure to water vapour and wet flue gas has been developed and demonstrated on very small samples, less than 10 mg. The methodology proposed, based on the use of the ZLC, has the key advantage of allowing to monitor each component of a flue gas mixture and allows to determine when saturation is achieved. Stability tests should be based on the prolonged exposure to an aggressive environment and, for reliable long-term data, exposures should aim to saturate the adsorbent with the critical contaminants.

The results obtained on the Ni-CPO-27 show a higher degree of deactivation than previously reported. It seems that the difference can be attributed to the actual amounts of SO<sub>2</sub> and H<sub>2</sub>O adsorbed on the materials during the stability tests. This indicates that stability tests should measure these quantities if phenomenological models are to be developed which can then be used to predict the extent of deactivation in full scale carbon capture units.

The experimental protocol based on the use of a ZLC system allows to determine also the time required to saturate the sample with contaminants. Moreover the use of a very small amount of sample (less than 10 mg) allows simultaneously to reduce the experimental time required as well as the gas consumption. As a result, the technique allows to determine in a few days the extent of the deactivation, with minimal consumption of gas. The protocol effectively “accelerates” the deterioration process of the adsorbent.

The results obtained on Mg-CPO-27 clearly indicate that this material is not stable to water. Even though this material has very large CO<sub>2</sub> capacities under dry conditions, it seems unlikely that it can find use in carbon capture applications given that the deactivation is not reversible. Any handling problem could require a complete replacement of the adsorbent in a real carbon capture system.

The Ni-CPO-27 was the more stable adsorbent retaining more than 80% of its original CO<sub>2</sub> capacity after the water stability test. On exposure to wet flue gas this material has a significant drop in capacity which indicates that either a SO<sub>x</sub> abatement system is needed or careful control of counter-current regeneration has to be implemented in the vacuum swing adsorption process with a sacrificial layer added to the adsorption bed to minimise the impact of impurities.

The ZLC was proven to be a valuable tool for deciding if impurities will influence the design of carbon capture systems based on novel adsorbents. Clearly further investigations should be carried out to better understand the deactivation/stabilisation mechanism of these adsorbents and this could lead to structural modifications which could help improve the resistance of the materials to impurities.



## References

1. C. W. Jones, S. Choi and J. H. Drese, *ChemSusChem*, 2009, **2**, 796 - 854.
2. P. D. C. Dietzel, V. Besikiotis and R. Blom, *Journal of Materials Chemistry*, 2009, **19**, 7362 - 7370.
3. S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *Journal of the American Chemical Society*, 2008, **130**, 10870 - 10871.
4. S. Majumdar, A. Sengupta, J. S. Cha and K. K. Sirkars, *Industrial & Engineering Chemistry Research*, 1994, **33**, 667 - 675.
5. J. Liu, Y. Wang, A. I. Benin, P. Jakubczak, R. R. Willis and M. D. LeVan, *Langmuir*, 2010, **26**, 14301 - 14307.
6. J. Liu, A. I. Benin, A. M. B. Furtado, P. Jakubczak, R. R. Willis and M. D. LeVan, *Langmuir*, 2011, **27**, 11451-11456.
7. S. Han, Y. Huang, T. Watanabe, Y. Dai, K. S. Walton, S. Nair, D. S. Sholl and J. C. Meredith, *ACS Combinatorial Science*, 2012, **14**, 263 – 267.S.
8. Han, Y. Huang, T. Watanabe, S. Nair, K. S. Walton, D. S. Sholl and J. Carson Meredith, *Microporous and Mesoporous Materials*, 2013, **173**, 86-91.
9. N. C. Burtch, H. Jasuja and K. S. Walton, *Chemical Reviews*, 2014, **114**, 10575-10612.
10. J. Liu, J. Tian, P. K. Thallapally and B. P. McGrail, *The Journal of Physical Chemistry C*, 2012, **116**, 9575 – 9581.
11. P. Kusgens, M. Rose, I. Senkovska, H. Frode, A. Henschel, S. Siegle and S. Kaskel, *Microporous and Mesoporous Materials*, 2009, **120**, 325 - 330.
12. P. M. Schoenecker, C. G. Carson, H. Jasuja, C. J. J. Flemming and K. S. Walton, *Industrial & Engineering Chemistry Research*, 2012, **51**, 6513 – 6519.
13. A. C. Kizzie, A. G. Wong-Foy and A. J. Matzger, *Langmuir*, 2011, **27**, 6368 - 6373.
14. T. G. Glover, G. W. Peterson, B. J. Schindler, D. Britt and O. M. Yaghi, *Chemical Engineering Science*, 2011, **66**, 163 - 170.
15. N. J. Hinks, A. C. McKinlay, B. Xiao, P. S. Wheatley and R. E. Morris, *Microporous and Mesoporous Materials*, 2010, **129**, 330 - 334.
16. B. Xiao, P. S. Wheatley, X. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, I. L. Megson, S. Bordiga, L. Regli, M. Thomas and R. E. Morris, *Journal of the American Chemical Society*, 2007, **129**, 1203 - 1209.
17. R. C. Huxford, J. Della Rocca and W. Lin, *Current Opinion in Chemical Biology*, 2010, **14**, 262 - 268.
18. F. Bonino, S. Chavan, J. G. Vitillo, E. Groppo, G. Agostini, C. Lamberti, P. D. C. Dietzel, C. Prestipino and S. Bordiga, *Chemistry of Materials*, 2008, **20**, 4957 - 4968.
19. J. Yu, Y. Ma and P. B. Balbuena, *Langmuir*, 2012, **28**, 8064 – 8071.
20. K. Yu, K. Kiesling and J. R. Schmidt, *The Journal of Physical Chemistry C*, 2012, **116**, 20480 – 20488.
21. P. D. C. Dietzel, R. Blom and H. Fjellvåg, *European Journal of Inorganic Chemistry*, 2008, 3624 - 3632.
22. P. D. C. Dietzel, P. A. Georgiev, J. Eckert, R. Blom, T. Strassle and T. Unruh, *Chemical Communications*, 2010, **46**, 4962 - 4964.
23. J. Kahr, R. E. Morris and P. A. Wright, *CrystEngComm*, 2013,**15**, 9779-9786.
24. X. Hu, S. Brandani, A. I. Benin and R. R. Willis, *Industrial & Engineering Chemistry Research*, 2015, **54**, 6772-6780.
25. F. Brandani, D. M. Ruthven and C. G. Coe, *Industrial & Engineering Chemistry Research*, 2003, **42**, 1451 - 1461.



26. S. Brandani and D. M. Ruthven, *Adsorption*, 1996, **2**, 133 - 143.
27. J. C. Abanades, B. Arias, A. Lyngfelt, T. Mattisson, D. E. Wiley, H. Li, M. T. Ho, E. Mangano and S. Brandani, *International Journal of Greenhouse Gas Control*, 2015, **40**, 126-166.
28. F. Brandani and D. M. Ruthven, *Industrial & Engineering Chemistry Research*, 2004, **43**, 8339-8344.
29. A. Ö. Yazaydin, R. Q. Snurr, T. H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low, and R. R. Willis, *Journal of the American Chemical Society*, 2009, **131 (51)**, 18198-18199.
30. Y. Jiao, C. R. Morelock, N. C. Burtch, W. P. Mounfield, III, J. T. Hungerford, and K. S. Walton, *Industrial & Engineering Chemistry Research*, 2015, **54 (49)**, 12408-12414.
31. D. Cattaneo, S. J. Warrender, M. J. Duncan, C. J. Kelsall, M. K. Doherty, P. D. Whitfield, I. L. Megson and R. E. Morris, *RSC Advances*, 2016, **6**, 14059-14067.
32. L. Ding and A. Ö. Yazaydin, *The Journal of Physical Chemistry C*, 2012, **116 (43)**, 22987-22991.
33. K. Yu and J.R. Schmidt, *The Journal of Physical Chemistry C*, 2013, **117 (6)**, 3192-3192.
34. D. M. Ruthven, *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 1984.
35. P. Li, J. Chen, J. Zhang and X. Wang, *Separation & Purification Reviews*, 2015, **44**, 19-27.
36. K. Tan, S. Zuluaga, Q. Gong, Y. Gao, N. Nijem, J. Li, T. Thonhauser and Y. J. Chabal, *Chemistry of Materials*, 2015, **27 (6)**, 2203-2217.